This document contains Appendix D from the 2004 Norwegian Star Data Report. Appendix D contains the sampling and analysis plan for Norwegian Star Sampling Episode 6504. The report and all the appendices for this sampling event can be downloaded from ***http://www.epa.gov/owow/oceans/cruise_ships/finalstar.html***

Norwegian Star

2004 Analytical Results

Appendix D

March 2006

Appendix D

DATA REVIEW NARRATIVES AND OTHER ISSUES

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6504

Data Validation Report For BOD_5 Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

December 22, 2004

BOD_5 Method 405.1

Completeness

During Sampling Episode 6504, a total of 30 samples (excluding QC samples) were collected for analysis of 5-day Biochemical Oxygen Demand (BOD_5) by EPA Method 405.1. All samples received by the laboratory were analyzed for BOD_5 for a completeness of 100% (all planned samples were collected and analyzed). Sample numbers for BOD_5 are provided in Table 1.

Table 1. BOD_5 Samples Collected During Sampling Episode 6504

Sample Numbers	Sample Point Description
65455, 65459, 65463, 65467, 65471	Treatment System Influent
65495, 65499, 65503, 65507, 65511, 65519, 65523, 65535	Treatment System Effluent
65415, 65419, 65423, 65427, 65431	Accommodations
65391, 65395, 65399, 65403, 65407	Galley
65435, 65439, 65443, 65447, 65451	Laundry
65411	Food Pulper
65547	Source Water

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete BOD_5 data for the samples listed in Table 1.

Holding Times

Method 405.1 requires that all BOD_5 samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates all BOD_5 samples received by the laboratory were analyzed within the 48 hour holding time.

Calibration

The calibration was performed with method blanks and glucose spiked blanks to verify seed effectiveness and analytical technique. Method blanks consist of potable water passed through an activated carbon bed to remove residual organic compounds. During Sampling Episode 6504, a total of 4 method blanks were prepared and analyzed for BOD_5. The results of the 4 method blank analysis shows the concentration of BOD_5 is less than 2 mg/L in each.

To verify seed effectiveness and analytical technique, method blanks were spiked with a sufficient amount of glucose to yield a theoretical BOD_5 concentration of 200 mg/L. Spiked

method blanks are then analyzed for BOD_5, and results of the analysis, reported as percent recovery, are compared to the recovery limits for Method 405.1. Table 2 shows the results of the spiked samples. Results of the spike sample analyses indicate all recoveries are within the method specified limits.

Table 2. Analysis of BOD_5 Recovery Data for Spiked Samples

Sample	Spike Result	Spike Level	Recovery	Recovery Limits
Method Blank	191 mg/L	200 mg/L	95.5%	60% - 140 %
Method Blank	183 mg/L	200 mg/L	91.5%	60% - 140%
Method Blank	149 mg/L	200 mg/L	74.5%	60% - 140%
Method Blank	147 mg/L	200 mg/L	73.5%	60% - 140%
Method Blank	171 mg/L	200 mg/L	85.5%	60% - 140%
Method Blank	174 mg/L	200 mg/L	87%	60% - 140%
Method Blank	188 mg/L	200 mg/L	94%	60% - 140%
Method Blank	190 mg/L	200 mg/L	95%	60% - 140%

Precision Analysis

Reproducibility for BOD_5 is measured as relative percent difference (RPD) between duplicate samples. Laboratory duplicate samples measure the precision of the method and analyst by comparing the results of two separate analyses on the same wastewater sample. Field duplicate samples measure the precision of the field sampling method by comparing the BOD_5 results for split wastewater samples prepared in the field. The QAPP for the Cruse Ship Rulemaking provides RPD targets for all laboratory duplicate samples and field duplicate samples as less than 20% and 30%, respectively.

Table 3 shows the RPD results for laboratory duplicate samples and duplicate method blank spiked samples. The RPDs shown in Table 3 indicate the four method blank spike duplicate samples are within the RPD, one laboratory duplicate sample (65499) is within the RPD, and one laboratory duplicate sample (65463) was outside the QAPP-specified target of less than 20%. Sample 65463 was collected from the influent to treatment and contained significant amounts of colloidal material and settleable solids. Slight differences in the distribution of these materials between duplicate laboratory samples could explain the RPD result being slightly outside the specified target; therefore, the associated variability is not considered unusual but the result is considered an estimated value.

Table 3. Relative Percent Difference Between Laboratory Duplicate Samples

Sample No.	BOD_5 Result	Duplicate BOD_5 Result	RPD	RPD Target
Spiked Method Blank	191 mg/L	183 mg/L	4.3%	<20%
Spiked Method Blank	149 mg/L	147 mg/L	1.4%	<20%
Spiked Method Blank	171 mg/L	174 mg/L	1.7%	<20%
Spiked Method Blank	188 mg/L	190 mg/L	1.1%	<20%
65499	4.67 mg/L	4.84 mg/L	3.6%	<20%
65463	659 mg/L	886 mg/L	**29%**	<20%

RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
RPDs outside the QAPP target are represented in bold.

Table 4 shows the RPD results for field duplicate samples. The RPDs shown in Table 4 indicate the field duplicate samples are within the QAPP-specified target of less than 30%; therefore, the field data precision is valid.

Table 4. Relative Percent Difference Between Field Duplicate Samples

Sample No.	BOD_5 Result	Sample No.	BOD_5 Result	RPD	RPD Target
65495	8.26 mg/L	65519	7.32 mg/L	12.1%	<30%
65499	4.67 mg/L	65523	5.16 mg/L	10.0%	<30%
65511	5.25 mg/L	65535	6.97 mg/L	28.2%	<30%

RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.

Data Quality Assessment

This data validation assessment indicates all the BOD_5 data collected during Sampling Episode 6504 can be used for the large cruise ship rulemaking effort.

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MEMORANDUM

DATE: January 17, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist
Sample Control Center

PC

SUBJECT: Data Review Narrative for Classical Analyses for the Alaskan Cruise Ship Industry, Episode 6504

OVERVIEW

Under EPA Contract Number 68-C-03-058, ProChem (formerly QBioChem) submitted classical wet chemistry data for 33 samples in Episode 6504. Table 1 provides a list of the samples, matrices, descriptions, sampling dates, and the required analytes.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analytes of Interest

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65391	Aqueous	SP1, Galley wastewater	8/09/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65395	Aqueous	SP1, Galley wastewater	8/10/04	
65399	Aqueous	SP1, Galley wastewater	8/11/04	
65403	Aqueous	SP1, Galley wastewater	8/12/04	
65407	Aqueous	SP1, Galley wastewater	8/13/04	
65411	Aqueous	SP2, Food pulper	8/10/04	
65415	Aqueous	SP3, Accommodations wastewater	8/09/04	
65419	Aqueous	SP3, Accommodations wastewater	8/10/04	
65423	Aqueous	SP3, Accommodations wastewater	8/11/04	
65427	Aqueous	SP3, Accommodations wastewater	8/12/04	
65431	Aqueous	SP3, Accommodations wastewater	8/13/04	
65435	Aqueous	SP4, Laundry wastewater	8/9/04	
65439	Aqueous	SP4, Laundry wastewater	8/10/04	
65443	Aqueous	SP4, Laundry wastewater	8/11/04	
65447	Aqueous	SP4, Laundry wastewater	8/12/04	
65451	Aqueous	SP4, Laundry wastewater	8/13/04	

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Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analytes of Interest

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65455	Aqueous	SP5, Influent to wastewater treatment	8/9/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65459	Aqueous	SP5, Influent to wastewater treatment	8/10/04	
65463	Aqueous	SP5, Influent to wastewater treatment	8/11/04	
65467	Aqueous	SP5, Influent to wastewater treatment	8/12/04	
65471	Aqueous	SP5, Influent to wastewater treatment	8/13/04	
65495	Aqueous	SP7, Effluent from wastewater treatment	8/09/04	
65499	Aqueous	SP7, Effluent from wastewater treatment	8/10/04	
65503	Aqueous	SP7, Effluent from wastewater treatment	8/11/04	
65507	Aqueous	SP7, Effluent from wastewater treatment	8/12/04	
65511	Aqueous	SP7, Effluent from wastewater treatment	8/13/04	
65519	Aqueous	SP8, Effluent from wastewater treatment	8/09/04	total cyanide
65523	Aqueous	SP8, Effluent from wastewater treatment	8/10/04	total cyanide
65527	Aqueous	SP8, Effluent from wastewater treatment	8/11/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide
65531	Aqueous	SP8, Effluent from wastewater treatment	8/12/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC
65535	Aqueous	SP8, Effluent from wastewater treatment	8/13/04	
65539	Solid	SP9, Biosludge	8/09/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TOC, total cyanide
65547	Aqueous	SP11, Source Water	8/11/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, total phosphorus, TKN, TDS, TSS, TOC, total cyanide

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004) and with the specifications listed in the analytical requirements summary for this episode. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the contract-specified holding times for all classical wet chemistry parameters specified in the sampling and analysis plan with the exception of 12 total organic carbon (TOC) samples, which were analyzed outside of the contract-specified holding time due to an instrument software problem, and one sample that was not analyzed for sulfate due to an oversight by the laboratory. The calibration and continuing calibration standards were successfully analyzed, where required by the methods. Laboratory blanks were performed for each analysis, and there was no contamination detected above the laboratory's reporting limits. The QC samples, including the ongoing and precision recovery sample (OPR) and matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

DATA ISSUES: SULFATE

Sample 65547 was not analyzed for sulfate due to an oversight by the laboratory. SCC did not initiate the analysis because the sample holding time had been exceeded by more than 30 days. Therefore, no sulfate data are reported in the database for sample 65547.

DATA ISSUES: TOTAL ORGANIC CARBON (TOC)

Holding Times

Twelve samples were analyzed for TOC 3 to 4 days after the holding time had expired, due to an instrument software problem at the laboratory. Therefore, SCC considers the TOC results for those samples to be estimated values. These samples are detailed in Table 2.

DATA ISSUES: AVAILABLE CYANIDE GREATER THAN TOTAL CYANIDE

For all samples in this episode, SCC evaluated total cyanide results against available cyanide results, and found that available cyanide was detected in samples 65395, 65411, 65455, 65459, 65463, 65467, and 65471, while total cyanide were not detected in these samples. In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. However, for these samples, it is important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the available cyanide determination was performed by a different laboratory. In addition, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results. Therefore, it may not be possible to identify problems that would invalidate one cyanide fraction or the other.

Three sets of MS/MSD samples were prepared for total cyanide analysis in Episode 6504 on samples 65519 (an effluent), 65523 (an effluent), and 65527 (accommodations wastewater), and all showed acceptable spike recoveries. Thus, there do not appear to be pervasive problems with the recovery of total cyanide in samples from this episode.

A comparison of the total cyanide results and available cyanide results for samples 65395, 65411, 65455, and 65459 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at approximately 22 to 36 µg/L.

Sample 65395 is listed as the galley wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65395 in the database, but flagging them to indicate the irreconcilable differences.

Samples 65455 and 65459 are influents to treatment and, as noted above, there are no MS/MSD analyses that demonstrate method performance for this matrix type. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65455 and 65459 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65411 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system, and as noted above, there are no MS/MSD data that demonstrate method performance for matrices other than effluents. During the review of the data, SCC noted that the traffic report for the aliquot of Sample 65411 for total cyanide analysis indicated that the aliquot was collected at 14:00 on 8/10/04, while the traffic report for the aliquot submitted for available cyanide analysis indicated that that aliquot was collected at 3:00 PM (15:00) on 8/11/04. This concern was resolved following discussions with EPA and the sampling contractor, whose field records indicated that both aliquots were collected at the same time, and that the one traffic report was incorrect. Having resolved the issue of the time of sample collection, but lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65411 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6504, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

The samples were analyzed for available cyanide by Bayer Laboratory. A separate data narrative has been prepared for the available cyanide analysis.

TECHNICAL NOTES:

Silica Gel Treated N-Hexane Extractable Material (SGT-HEM)

Samples 65495, 65499, and 65503 were not analyzed for SGT-HEM because the HEM results were non-detects. At EPA's request, SCC created SGT-HEM records in the database, with the results for SGT-HEM are reported as "NA," with the SCC qualifier reading "Not analyzed due to non-detect HEM result."

If you have any questions regarding the analyses of these samples or the review of these data, please contact me by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6504 **Analysis:** Classicals

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65547	sulfate	No data in the database	Sample was not analyzed due to a laboratory oversight	Exclude	N/A
65391	TOC	Estimated value	Holding time exceeded	NA	645 mg/L
65395	TOC	Estimated value	Holding time exceeded	NA	252 mg/L
65411	TOC	Estimated value	Holding time exceeded	NA	1560 mg/L
65415	TOC	Estimated value	Holding time exceeded	NA	70.8 mg/L
65419	TOC	Estimated value	Holding time exceeded	NA	44.8 mg/L
65435	TOC	Estimated value	Holding time exceeded	NA	41.1 mg/L
65439	TOC	Estimated value	Holding time exceeded	NA	36.7 mg/L
65455	TOC	Estimated value	Holding time exceeded	NA	192 mg/L
65459	TOC	Estimated value	Holding time exceeded	NA	112 mg/L
65495	TOC	Estimated value	Holding time exceeded	NA	13.6 mg/L
65499	TOC	Estimated value	Holding time exceeded	NA	12 mg/L
65539	TOC	Estimated value	Holding time exceeded	NA	62,000 mg/L
65395, 65411, 65455, 65459, 65463, 65467, 65471	total cyanide	Irreconcilable results for total and available cyanide	Results for available cyanide greater than total cyanide	IRR	ND

ND = Non-detect at the laboratory's reporting limit. See the level in the database.
NA = Not applicable
MIN = Minimum value
IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.

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MEMORANDUM

DATE: March 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Jody Donnelly, Quality Assurance Chemist JHD
Sample Control Center

SUBJECT: Data Review Narrative for Dioxin/Furan Analysis for the Alaskan Cruise Ship Industry, Episode 6504

OVERVIEW

Under CSC Purchase Order 637415SSD, Axys Analytical Services submitted data for the analysis of dioxins and furans by EPA Method 1613B for one solid sample in Episode 6504. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6504	65556	Solid	SP10, Incinerator ash	08/12/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxin/Furan Analysis by Method 1613B (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

The sample was successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable.

Reporting Limits

The sample was extracted using approximately 5 grams instead of the method-specified 10 grams. As a result, the minimum levels (MLs) provided in the database for sample 65556 increased by approximately a factor of 2. The laboratory's past experience with ash samples shows that they tend to have significant matrix interference, which is why the sample size was reduced. Because the laboratory calibrated their instrument to 5 times lower than the lowest calibration standard specified in Method 1613B, the difference in sample size has no impact on the quality of the data. The MLs provided in the database for these samples reflect the smaller sample size.

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Some analytes in sample 65556 were qualified by SCC with a “J” flag, which indicates an estimated result that is below the laboratory’s reporting limit but above the method detection limit. These analytes are annotated as such in the database and are detailed in Table 2.

If you have any questions regarding the analysis of this sample or the review of these data, please contact me, by telephone at (703) 461-2203 or by facsimile at (703) 461-8056.

Attachment

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6504 **Analysis:** Method 1613B

Industry: Alaskan Cruise Ship **Reviewer:** J. Donnelly

Sample	Analyte	Action	Reason	SCC Qual	Level (ng/kg)
65556	2,3,4,7,8-PeCDF	Estimated value	Analyte detected below laboratory's reporting limit but above method detection limit	J	5.16
	1,2,3,4,7,8-HxCDF				8.51
	2,3,4,6,7,8-HxCDF				4.51
	1,2,3,4,6,7,8- HpCDD				7.69
	OCDD				13.58

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MEMORANDUM

DATE: January 27, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist
Sample Control Center

PC

SUBJECT: Data Review Narrative for Dioxin/Furan Analyses for the Alaskan Cruise Ship Industry
Episode 6504

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of dioxins/furans by EPA Method 1613B for one aqueous sample in Episode 6504. Table 1 provides a list of the sample, matrix, sample description, sampling date, and the required analytical method.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6504	65435	Aqueous	SP4, Laundry Wastewater	8/09/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxin/Furan Analyses (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with the sample. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

Sample 65435 was successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. Instead of using the method-specified clean up procedure, the sample was processed by an automated clean up procedure that employs the Fluid Management System Inc., *"Power-Prep™ System,"* using standard chromatographic clean up columns. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable. None of the dioxins/furans were detected in this sample.

Reporting Limits

The laboratory's reporting limits are at the method-specified minimum levels (MLs). The sample was extracted using less than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the MLs for sample 65435 by 55%. The MLs provided in the database for this sample reflect the smaller sample volume.

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If you have any questions regarding the analyses of this sample or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6504

Data Validation Report For Microbiological Analyses

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

January 27, 2005

Enterococci by MPN Method ASTM D6503-99
Fecal Coliform by MF SM 9222D
***E. Coli* by MPN Enzyme Substrate SM 9223B**

Completeness

During Sampling Episode 6504, a total of 82 samples (excluding QC samples) were collected for analysis of enterococci, fecal coliform, and *E. coli* by the methods listed above. Sample numbers ranged between 65391 and 65560. The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete microbiological data for all submitted samples. A list of the samples collected and analyzed during Sampling Episode 6504 is provided in Table 1.

Table 1. List of Samples and Required Microbiological Analyses for Sampling Episode 6504

Sample Numbers	Sample Point Description
65391, 65392, 65395, 65396, 65399, 65400, 65403, 65404, 65407, 65408	Galley Wastewater
65411	Food Pulper Wastewater
65415, 65419, 65420, 65423, 65424, 65427, 65428, 65431, 65432	Accommodations Wastewater
65435, 65436, 65439, 65440, 65443, 65444, 65447, 65448, 65451, 65452	Laundry Wastewater
65455, 65456, 65457, 65459, 65460, 65463, 65464, 65465, 65467, 65468, 65469, 65471, 65472, 65473	Treatment System Influent
65475, 65476, 65477, 65479, 65480, 65481, 65483, 65484, 65485, 65487, 65488, 65489, 65491, 65492, 65493	Influent to UV Disinfection
65495, 65496, 65497, 65499, 65500, 65501, 65503, 65504, 65505, 65507, 65508, 65509, 65511, 65512, 65513, 65519, 65523, 65527, 65531, 65558, 65559, 65560	Treatment System Effluent
65547	Source Water

According to the Quality Assurance Project Plan (QAPP) developed for the Rulemaking Support for Large Cruise Ships in Alaska Waters, sampling completeness is the number of valid samples collected relative to the number of samples planned for collection; analytical completeness is the number of valid sample measurements relative to the number of valid samples collected; and overall completeness is the number of valid sample measurements relative to the number of samples planned for collection. For the cruise ship sampling program a

minimum goal of 90% completeness for sampling and analytical completeness has been established, and a minimum goal of 81% for overall completeness (determined by multiplying sampling and analytical completeness goals) has been established.

The number of samples actually collected onboard the Norwegian Star was less than that described in the ship-specific Sampling and Analysis Plan. First, to conserve laboratory capacity, one rather than two grab samples of food pulper wastewater were collected. Characterizing food pulper wastewater is a secondary objective of the sampling program, and this sample is a complex matrix with high solids content. Second, one rather than two accommodations wastewater grab samples were collected on the first sampling day due to lack of flow at this sampling point. Finally, two rather than three influent to treatment grab samples were collected on the second sampling day due to sampler error. As a result, sampling completeness was 96% for Sampling Episode 6504.

For enterococci and *E. coli* for Sampling Episode 6504, all 82 samples collected were analyzed and all results are valid, resulting in a laboratory completeness of 100% for these microorganisms. For fecal coliform, 12 of the samples collected were contaminated by a rinse water bottle making the data invalid (see discussion under ***Dilution Water Sterility Checks*** below for additional information). In addition, one fecal coliform sample had matrix effects, making the data from this sample invalid (see discussion under **Detection Limits** below for additional information). For fecal coliform, 69 of the 82 total samples yielded valid data, resulting in a laboratory completeness of 84%, which is short of the 90% goal.

Overall completeness for enterococci and *E. coli* was 96%, which achieves the 81% goal. For fecal coliform, overall completeness was approximately 81%, just achieving the 81% goal.

Holding Times

The QAPP developed for the cruise ship rulemaking requires all microbiological samples be analyzed within 6 hours following collection. Analysis of traffic reports and laboratory data sheets indicates all microbiological samples submitted field laboratory for analysis were analyzed within 6 hours following collection.

Detection Limits

Some microbiological results were reported by Analytica Alaska as "greater than" a specified value (e.g., >600,000,000 CFU/100 mL). These results are qualified in the analytical database by a ">" flag and are listed in Table 2. This qualifier indicates the sample was not diluted sufficiently (i.e., the measured concentration exceeds the range of dilutions). The reported results in the database are the upper limit of the measurement range, and the ">" flag indicates that the actual concentrations are some level greater than the reported upper limit. Although the results are valid, data users should consider this data qualification in using the data.

Table 2. Microbiological Sample Results with ">" Qualifier

Analysis	Sample Numbers
Enterococci	65392, 65411, 65419, 65443
Fecal Coliform	65391, 65392, 65396, 65399, 65415, 65419, 65423, 65439, 65443, 65463, 65464, 65483, 65484
E. Coli	65391, 65396, 65399, 65400, 65407, 65411, 65415, 65419, 65420, 65423, 65424, 65427, 65428, 65472

During onboard analysis, some samples were overly diluted to levels which generated non-detect (ND) results, but with detection limits much greater than both their expected concentrations in these samples and the typical detection limits of 1 MPN/100 ml for *E. coli* and enterococci and 2 CFU/100 ml for fecal coliform. A list of the samples that were overly diluted and their associated detection limits are provided in Table 3.

Table 3. Samples Reported With Excessively High Detection Limits

Sample No.	Microbiological	Result	Detection Limit	Sample Description
65456	*E. Coli*	ND	10,000 MPN/100ml	Influent to Treatment
65475	*E. Coli*	ND	10,000 MPN/100ml	Influent to UV Disinfection
65476	*E. Coli*	ND	10,000 MPN/100ml	Influent to UV Disinfection
65477	*E. Coli*	ND	10,000 MPN/100ml	Influent to UV Disinfection
65479	*E. Coli*	ND	10,000 MPN/100ml	Influent to UV Disinfection
65480	*E. Coli*	ND	10,000 MPN/100ml	Influent to UV Disinfection
65475	Enterococci	ND	10,000 MPN/100ml	Influent to UV Disinfection
65476	Enterococci	ND	10,000 MPN/100ml	Influent to UV Disinfection
65477	Enterococci	ND	10,000 MPN/100ml	Influent to UV Disinfection
65479	Enterococci	ND	10,000 MPN/100ml	Influent to UV Disinfection
65480	Enterococci	ND	10,000 MPN/100ml	Influent to UV Disinfection
65477	Fecal Coliform	ND	1,000 CFU/100ml	Influent to UV Disinfection
65479	Fecal Coliform	ND	1,000 CFU/100ml	Influent to UV Disinfection

Although the results from the samples shown in Table 3 are valid, their use for engineering analysis is limited due to the high detection limits.

One additional sample (Sample No. 65395) analyzed for fecal coliform resulted in a high detection limit (10,000 CFU/100 ml), and the sample result was reported by the laboratory as 10,000 CFU/100 mls. Discussions with the laboratory analyst determined the sample was collected from the galley wastewater steam and that matrix effects had impacted the sample result. As such, this sample result is not considered valid and will be excluded from the analytical database.

Calculation of Fecal Coliform Density

Fecal coliform density should be computed from sample quantities that produced membrane filtration counts within the desired range of 20 to 60 fecal coliform colonies. This was not always possible for many cruise vessel samples for various reasons. First, many samples, such as wastewater treatment effluent samples, had low concentrations of microbial contaminants, and the occurrence of fecal coliform colonies was minimal. In these cases, as specified by the method, the analyst counted all fecal coliform colonies, disregarding the lower limit of 20.

Second, most samples (other than wastewater treatment effluent) required a series of sample dilutions to obtain between 20 and 60 colony forming units per filter pad. In most cases, the analyst obtained a result within this range using one of the prepared dilutions. However, in a few instances, no single filter generated a result within the desired range (i.e., two results within the desired range, two results either above or below the desired range, one result above and one result below the desired range, etc.). In these cases, as specified by the method, the analyst totaled the counts on the two filters and reported the result as a number per 100 mL. Table 4 lists the fecal coliform samples for Sampling Episode 6504 that did not yield a single result within the desired range, and for which the analyst computed the number of colony forming units based on a calculation of the results from multiple plates. Calculations for these samples are provided in the Cruise Ship Rulemaking Record.

Table 4. Fecal Coliform Samples For Which Multiple Plates Were Used to Compute CFU/mL

Sample No.	Sample Description
65407	Galley Wastewater
65408	Galley Wastewater
65440	Laundry Wastewater
65480	Influent to UV Disinfection
65491	Influent to UV Disinfection

Sample No.	Sample Description
65493	Influent to UV Disinfection

In summary, calculation of fecal coliform density was performed as specified by the method, and the reported results are valid.

Laboratory QC Measures

QC measures for microbiologicals include positive and negative controls, media sterility checks, dilution water sterility checks, sample bottle blanks, membrane filter preparation blanks, and verification of incubator temperatures. The following describes the results of each of these QC checks used during Sampling Episode 6504. (The actual QC results are contained in Analytica Alaska's laboratory report, which is provided in the Cruise Ship Rulemaking Record.)

Positive and Negative Controls

Positive and negative controls are known cultures that are analyzed exactly like the field samples, and will produce an expected positive or negative result for a given type of medium. For Sampling Episode 6504, one medium-specific positive and negative control was analyzed for each media lot used. Results of the positive and negative controls indicate the media used by the field laboratory for Sampling Episode 6504 produced expected results.

Media Sterility Checks

Media are checked for sterility by incubating the media at the appropriate temperature without sample and observed for growth. For Sampling Episode 6504, one medium sterility check was performed for each medium lot used. The media sterility check verified the media used by the field laboratory had not been contaminated with any of the microorganisms being analyzed for this work.

Dilution Water Sterility Checks

Dilution water is analyzed exactly like a field sample and observed for growth of fecal coliform, *E. coli*, and enterococci to verify the water is not contaminated with these organisms prior to use. For Sampling Episode 6504, one sample dilution blank was analyzed for each lot of dilution water used. Results of dilution water blank analysis verified the water had not been contaminated with any of the microorganisms being analyzed for this work.

During on-board analysis of fecal coliform, the analyst began to notice unusually high results for samples that typically contain low numbers of colony forming units (CFUs). Further investigation revealed that sterile water was transferred to a rinse bottle that had become contaminated by fecal coliform. The samples that were impacted by the contaminated rinse bottle are listed in Table 5.

Table 5. Fecal Coliform Samples Impacted By Contaminated Rinse Bottle

Sample No.	Sample Description
65400	Galley Wastewater
65403	Galley Wastewater
65424	Accommodations Wastewater
65427	Accommodations Wastewater
65444	Laundry Wastewater
65447	Laundry Wastewater
65465	Influent to Treatment
65467	Influent to Treatment
65485	Influent to UV Disinfection
65487	Influent to UV Disinfection
65505	Final Effluent
65507	Final Effluent

Fecal coliform results for these samples are suspect and should not be used for the cruise ship rulemaking effort. Accordingly, these sample results will be excluded from the analytical database.

Sample Bottle Blank

A sample bottle blank was analyzed for each bottle lot used during Sampling Episode 6504 to determine adequate bottle sterilization prior to use by the sampling crew. Results of the sample bottle blank (dilution water poured into the sample bottle and analyzed) verified the sample bottles had not been contaminated with any of the microorganisms being analyzed for this work.

Membrane Filter Preparation Blank

Membrane filter blanks were analyzed at the beginning of each set of filtered samples to document adequate sterilization of membrane filtration equipment. Membrane blanks verified that the equipment used for filtration during Sampling Episode 6504 had not been contaminated with any of the microorganisms being analyzed for this work.

Incubator Temperature

Incubator temperatures were monitored in the onboard laboratory to verify that prepared microbiological samples were being incubated at the correct temperatures. Review of the laboratories incubator log sheets verified the temperature was measured and recorded twice daily, no less than four hours apart, and the temperature checks were ±0.5°C apart.

Precision Analysis

Reproducibility for the microbiological analyses is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking presents the target RPDs for all laboratory and field duplicate samples as less than 20% and 30%, respectively. During Sampling Episode 6504, additional 100-ml sample volumes were collected for three grab samples with the intent that the laboratory would prepare a single composite and then analyze duplicate samples from the composite to evaluate laboratory precision (i.e., laboratory duplicates). The laboratory did not prepare a composite, but instead analyzed each of the 100-ml sample volumes individually. Because a composite was not prepared, laboratory precision could not be evaluated. The results obtained from analysis of these three individual sample volumes are field duplicates, not laboratory duplicates, and because they were collected as laboratory duplicates, the original sample and the duplicate sample have the same sample number. In order to differentiate the original from the duplicate, ERG assigned new SCC numbers (65558, 65559, and 65560) to the duplicate samples.

During Sampling Episode 6504, four additional sets of intended field duplicate samples (i.e., different sample numbers) were also collected and analyzed by each of the three microbiological methods. These field duplicate samples were prepared to determine the precision of the field sampling equipment. Duplicate sample data for the samples described above, along with the four intended field duplicate samples, are provided for *E. coli*, fecal coliform, and enterococci in Tables 6, 7 and 8, respectively.

Table 6. *E. Coli* Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65495	65519	ND	ND	NA	<30%
65499	65523	ND	ND	NA	<30%
65503	65527	ND	ND	NA	<30%
65507	65531	ND	ND	NA	<30%
65496	65558*	ND	ND	NA	<30%
65500	65559*	ND	ND	NA	<30%

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65508	65560*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 MPN/100 ml.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

Table 7. Fecal Coliform Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65495	65519	ND	ND	NA	<30%
65499	65523	ND	ND	NA	<30%
65503	65527	ND	ND	NA	<30%
65507	65531	>600 CFU/100mL**	ND	NA	<30%
65496	65558*	ND	ND	NA	<30%
65500	65559*	ND	ND	NA	<30%
65508	65560*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 2 CFU/100ml.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.
**Sample contaminated and results are unusable.

Table 8. Enterococci Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65495	65519	ND	ND	NA	<30%
65499	65523	ND	ND	NA	<30%
65503	65527	ND	ND	NA	<30%
65507	65531	ND	ND	NA	<30%
65496	65558*	ND	ND	NA	<30%
65500	65559*	ND	ND	NA	<30%
65508	65560*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 MPN/100 ml.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

The data provided in Tables 6, 7, and 8 show that nearly all of the field duplicate samples analyzed by the laboratory gave nearly the same measured values. One duplicate fecal coliform analysis (sample no. 65507) contained >600 CFU/100 ml; however, the laboratory noted this sample had been contaminated by the rinse bottle as discussed previously. Results from this sample are not valid. Although the RPDs could not be calculated because one or both of the duplicate sample results was less than the laboratory reporting limit, the microbiological analysis precision is acceptable for this program, and the reported microbiological results are valid.

Data Quality Assessment

This data validation assessment indicates the microbiological data collected during Sampling Episode 6504 can be used for the large cruise ship rulemaking effort, with the exceptions of those samples contaminated by the sterile water rinse bottle and the galley wastewater sample which provided erroneous results due to matrix effects.

Data users should consider limitations of sample results derived from overly high or low sample dilution as they use the data.

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MEMORANDUM

DATE: January 27, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Julie Dixon Rest, Quality Assurance Chemist JDR
Sample Control Center

SUBJECT: Data Review Narrative for Total and Dissolved Metals Analyses for the Alaskan Cruise Ship Industry, Episode 6504

OVERVIEW

Under EPA contract number 68-C-03-044, ProChem Analytical (formerly Q BioChem) submitted data for the analysis of total and dissolved metals by EPA Methods 200.7, 200.9, 245.1, and 245.5 in Episode 6504. The 31 aqueous samples and 2 solid samples in this episode were analyzed for 25 metals by Method 200.7 (ICP-AES) and thallium by Method 200.9 (GFAA). Mercury analyses of the aqueous samples were performed by Method 245.1, and by Method 245.5 for the solid samples. Table 1 provides a list of samples, matrices, descriptions, sampling dates, and the required analytical methods.

All 31 aqueous samples were analyzed for total metals and 30 out of 31 aqueous samples were analyzed for dissolved metals. The two solid samples were analyzed for total metals. The laboratory added the suffixes "D" and "T" to the sample numbers on the hard copy results to differentiate the analyses for dissolved metals and total metals, respectively. These suffixes are also used in this data review narrative. However, the sample numbers in the database will not contain these suffixes. Consistent with current EAD protocols, the total and dissolved metals distinctions are provided in the "procedure" field of the database.

This episode included data for four matrix spike/matrix spike duplicate MS/MSD pairs for aqueous effluent samples. Of these, all four were analyzed for total metals and three were analyzed for dissolved metals.

Table 1 - Sample Identifiers, Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65391	Aqueous	SP1, Galley wastewater	8/09/04	200.7, 200.9, and 245.1
65395	Aqueous	SP1, Galley wastewater	8/10/04	
65399	Aqueous	SP1, Galley wastewater	8/11/04	
65403	Aqueous	SP1, Galley wastewater	8/12/04	
65407	Aqueous	SP1, Galley wastewater	8/13/04	
65411	Aqueous	SP2, Food pulper	8/10/04	
65415	Aqueous	SP3, Accommodations wastewater	8/09/04	
65419	Aqueous	SP3, Accommodations wastewater	8/10/04	
65423	Aqueous	SP3, Accommodations wastewater	8/11/04	200.7, 200.9, and 245.1
65427	Aqueous	SP3, Accommodations wastewater	8/12/04	

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Table 1 - Sample Identifiers, Descriptions, and Analysis Methods				
EPA Sample #	**Matrix**	**Sample Description**	**Sampling Date**	**Methods**
65431	Aqueous	SP3, Accommodations wastewater	8/13/04	200.7, 200.9, and 245.1
65435	Aqueous	SP4, Laundry wastewater	8/09/04	
65439	Aqueous	SP4, Laundry wastewater	8/10/04	
65443	Aqueous	SP4, Laundry wastewater	8/11/04	
65447	Aqueous	SP4, Laundry wastewater	8/12/04	
65451	Aqueous	SP4, Laundry wastewater	8/13/04	
65455	Aqueous	SP5, Influent to wastewater treatment	8/9/04	
65459	Aqueous	SP5, Influent to wastewater treatment	8/10/04	
65463	Aqueous	SP5, Influent to wastewater treatment	8/11/04	
65467	Aqueous	SP5, Influent to wastewater treatment	8/12/04	
65471	Aqueous	SP5, Influent to wastewater treatment	8/13/04	
65495	Aqueous	SP7, Effluent from wastewater treatment	8/09/04	
65499	Aqueous	SP7, Effluent from wastewater treatment	8/10/04	
65503	Aqueous	SP7, Effluent from wastewater treatment	8/11/04	
65507	Aqueous	SP7, Effluent from wastewater treatment	8/12/04	
65511	Aqueous	SP7, Effluent from wastewater treatment	8/13/04	
65519	Aqueous	SP8, Effluent from wastewater treatment	8/09/04	
65523	Aqueous	SP8, Effluent from wastewater treatment	8/10/04	
65531	Aqueous	SP8, Effluent from wastewater treatment	8/12/04	
65539	Solid	SP9, Biosludge	8/09/04	200.7, 200.9 and 245.5
65547	Aqueous	SP11, Source water	8/11/04	200.7, 200.9, and 245.1
65555	Aqueous	SP13, Equipment blank	8/09/04	
65556	Solid	SP10, Incinerator Ash	8/12/04	200.7, 200.9 and 245.5

These data have been reviewed in accordance with SCC's Data Review Guidelines for Metals Analyses (November 2004) and with the specifications listed in EPA Method 200.7 (Rev. 5), 200.9 (Rev. 2.2), 245.1 (03/83), and 245.5 (03/83). All data are of acceptable quality with the qualifiers described below and detailed in the data review summary table (Table 2).

Following SCC's initial review of the data, EPA inquired about modifying the reporting convention used for metals to address EPA's need to compare sample results to the water quality criteria for Alaskan

coastal waters. The current EAD metals contracts specify that the laboratory report results down to the minimum level (ML) for each analyte. By examining both the hard copy raw data and the laboratory's electronic submission, SCC determined that results between the ML and the method detection limit (MDL) were available for all of the metals. After consultation with EPA, SCC modified the reported results such that any analytes not detected in the sample were reported as a non-detect at the laboratory's MDL rather than at the ML. As a result, there are also some analytes that are reported as detected between the ML and the laboratory's MDL. These results are flagged "J" in the database. This change also means that the hard copy data reported by the laboratory may not match the results in the database for values in the database between the MDL and ML of the analyte. This change also necessitated an additional review of all of the blank results to ensure that the low-level results reported in samples were not simply artifacts of the blanks.

SUMMARY

All 33 samples were successfully analyzed within the method-specified holding times. The initial precision and recovery (IPR) analyses and the method detection limit (MDL) study were performed and met the acceptance criteria, with the exception of aluminum and titanium MDL for solids. The laboratory MDL study for solid samples showed that the MDL values for aluminum and titanium exceeded method-specified limits or the minimum levels (MLs), at 15.5 mg/kg and 1.42 mg/kg, versus 5.0 mg/kg and 1.0 mg/kg, respectively. Since the aluminum and titanium results for solids are detected well above the MDLs, the data quality is not affected.

Calibration curves, calibration standards, and calibration blanks were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits, with the exceptions noted below and detailed in Table 2. QC samples, including laboratory control sample (LCS), matrix spike (MS) sample, matrix duplicate (MSD) sample, and laboratory serial dilution sample demonstrated that laboratory performance for these analyses was acceptable, with the exception of the issues described below.

DATA ISSUES

Blanks

One or more elements were detected in the preparation blanks and some of the continuing calibration blanks (CCBs) associated with the samples in this episode at concentrations greater than the respective MDLs but less than the method-specified MLs. (Note: This is a function of the change in reporting limits requested by EPA after the fact and not an issue of laboratory performance.) The data quality is affected as follows:

- Sample Results Less than Five Times Blank Results: When the sample result is less than five times the blank result, there are no means by which to ascertain whether or not the presence of the analyte may be attributed to contamination. Therefore, SCC recommends that the data be reported in the database as a non-detect at the MDLs, adjusted sample size, dilution, and matrices. These instances are detailed in the attached data review summary table.

- Sample Results Greater than Five Times but Less than Ten Times Blank Results: SCC considers these results to be of acceptable quality, but they may be maximum values. These instances are detailed in the attached data review summary table.

- Sample Results Greater than Ten Times Blank Results or Analyte Not Detected in Sample: SCC does not consider the presence of the analyte in the blank to adversely affect the data in cases

where the sample results are greater than ten times the associated blank results or where the analyte is not detected in associated samples. Because SCC considers such data to be acceptable without qualification, these cases do not merit further detail.

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Zinc (Zn) was recovered below the method-specified criteria in the MS, and the relative percent difference (RPD) between the MS and MSD exceeded the acceptance criteria for sample 65223T. Therefore, SCC considers the Zn result in this sample to be an estimated value.

Serial Dilutions

For aluminum (Al) in sample 65531, the percent difference (%D) between the original analysis and the dilution exceeded the method-specified criteria. Therefore, SCC considers the sample result for Al in sample 65531T to be an estimated value.

Sodium

Dilutions were required for sodium in sample 65411. For sample 65411, the result for dissolved sodium (780,000 µg/L), was significantly greater than the result for total sodium (402,000 µg/L). The laboratory reanalyzed the sample to confirm the original results. Since the total and dissolved sodium results for this sample vary by such a great amount, SCC recommends excluding both results from the database.

TECHNICAL NOTES

Some of these samples required dilutions due to matrix interferences or high levels of target analytes. The MDLs, as reported by the laboratory, reflect the dilutions.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachment

cc: Marla Smith, EPA
Beverly Randolph, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodie King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6504 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65523	Zn	Estimated value	MS recovery below method-specified criteria and the RPD between the MS and MSD exceeded criteria	NA	749 µg/L
Total 65531	Al	Estimated value	%D for serial dilution exceeded criteria	NA	272 µg/L
Total/Dissolved 65411	Na	Excluded from database	Dissolved result is significantly greater than total result	Exclude	NA
Dissolved 65419, 65439	Al	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Total 65419, 65423, 65431, 65439, 65443, 65451	Al	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Dissolved 65423, 65443	Al	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total 65427	Al	Report in database as non detect	Sample result < 5x blank result	NA	ND
Solid 65539, 65556	As	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total 65391	Be	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Total 65395, 65399, 65415, 65419, 65423, 65435, 65439, 65443, 65523, 65555	Be	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total/Dissolved 65427, 65431, 65447, 65451, 65547	B	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total/Dissolved 65403, 65467, 65471, 65503, 65507, 65511, 65531	B	Maximum value	Sample result > 5x and <10x blank result	NA	See database report

Table 2
Data Review Summary Table

Episode: 6504 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65395, 65419, 65435, 65439, 65455, 65459	Cd	Report in database as non detect	Sample result < 5x blank result	NA	ND
Solid 65539	Cd	Report in database as non detect	Sample result < 5x blank result	NA	ND
Solid 65556	Cd	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Total 65391	Cd	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Total 65555	Ca	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total 65443, 65555	Fe	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Dissolved 65395, 65399, 65411, 65415, 65419, 65423, 65435, 65439, 65443, 65459, 65463, 65495, 65499, 65523, 65555	Pb	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total 65407, 65427, 65431, 65447, 65451, 65467, 65471, 65507, 65511, 65531	Pb	Report in database as non detect	Sample result < 5x blank result	NA	ND
Dissolved 65547, 65555	Mn	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Total/Dissolved 65555	Na	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total 65419	Tl	Report in database as non detect	Sample result < 5x blank result	NA	ND
Dissolved 65403, 65407, 65427, 65447, 65451, 65467, 65471	Sn	Report in database as non detect	Sample result < 5x blank result	NA	ND

Table 2
Data Review Summary Table

Episode: 6504 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Solid 65539	Sn	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Total 65391, 65399, 65411, 65455, 65459, 65463	V	Report in database as non detect	Sample result < 5x blank result	NA	ND
Total 65547	Zn	Maximum value	Sample result > 5x and <10x blank result	NA	See database report
Dissolved 65547	Zn	Report in database as non detect	Sample result < 5x blank result	NA	ND

NA = Not applicable
ND = Not detected

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MEMORANDUM

DATE: February 15, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Julie Rest, Quality Assurance Chemist
Sample Control Center

SUBJECT: **Revised** Data Review Narrative for Organics Analyses for the Alaskan Cruise Ship Industry, Episode 6504

OVERVIEW

*The January 27th version of this narrative was revised to correct the omission of the methods listed for some samples in Table 1. The changes are shown in **bold**.*

Under EPA Contract Number 68-C-03-033, Ecology and Environment (E&E) submitted data for the analysis of volatiles by Method 624 and for semivolatile organics by Method 625 in Episode 6504. Table 1 provides a list of samples, sample descriptions, matrices, sampling dates, and the required analytical methods. This episode included twenty-nine aqueous samples for Method 624 analysis; and three solid samples and twenty-one aqueous samples for Method 625 analysis. The package included data for three matrix spike (MS) and matrix spike duplicate (MSD) pairs for Method 625 analysis, and two MS/MSD pairs for Method 624 analysis.

Table 1 - Sample Identifiers Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65391	Aqueous	SP1, Galley wastewater	8/09/04	624, 625
65395	Aqueous	SP1, Galley wastewater	8/10/04	624, 625
65399	Aqueous	SP1, Galley wastewater	8/11/04	624, 625
65403	Aqueous	SP1, Galley wastewater	8/12/04	624, **625**
65407	Aqueous	SP1, Galley wastewater	8/13/04	624, **625**
65411	Aqueous	SP2, Food pulper	8/10/04	624, 625
65415	Aqueous	SP3, Accommodations wastewater	8/09/04	624, 625
65419	Aqueous	SP3, Accommodations wastewater	8/10/04	624,625

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Table 1 - Sample Identifiers Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65423	Aqueous	SP3, Accommodations wastewater	8/11/04	624, 625
65427	Aqueous	SP3, Accommodations wastewater	8/12/04	624, **625**
65431	Aqueous	SP3, Accommodations wastewater	8/13/04	624, **625**
65435	Aqueous	SP4, Laundry wastewater	8/9/04	624, 625
65439	Aqueous	SP4, Laundry wastewater	8/10/04	624, 625
65443	Aqueous	SP4, Laundry wastewater	8/11/04	624, 625
65447	Aqueous	SP4, Laundry wastewater	8/12/04	624, **625**
65451	Aqueous	SP4, Laundry wastewater	8/13/04	624, **625**
65455	Aqueous	SP5, Influent to wastewater treatment	8/9/04	624, 625
65459	Aqueous	SP5, Influent to wastewater treatment	8/10/04	**624,** 625
65463	Aqueous	SP5, Influent to wastewater treatment	8/11/04	624, 625
65467	Aqueous	SP5, Influent to wastewater treatment	8/12/04	624, **625**
65471	Aqueous	SP5, Influent to wastewater treatment	8/13/04	624, **625**
65495	Aqueous	SP7, Effluent from wastewater treatment	8/09/04	624, 625
65499	Aqueous	SP7, Effluent from wastewater treatment	8/10/04	624, 625
65503	Aqueous	SP7, Effluent from wastewater treatment	8/11/04	624, 625
65507	Aqueous	SP7, Effluent from wastewater treatment	8/12/04	624, **625**
65511	Aqueous	SP7, Effluent from wastewater treatment	8/13/04	624, **625**
65519	Aqueous	SP8, Effluent from wastewater treatment	8/09/04	624, 625
65523	Aqueous	SP8, Effluent from wastewater treatment	8/10/04	624, 625
65527	Aqueous	SP8, Effluent from wastewater treatment	8/11/04	624, 625
65539	Solid	SP9, Biosludge	8/09/04	**624,** 625
65543	Solid	SP10, Incinerator ash	8/09/04	625
65547	Aqueous	SP11, Source water	8/11/04	624, **625**
65551	Aqueous	Trip blank	8/06/04	624
65555	Aqueous	SP13, Equipment blank	8/09/04	625
65556	Solid	SP10, Incinerator ash	8/12/04	625

These data have been reviewed in accordance with SCC's Data Review Guidelines for Volatile and Semivolatile Analysis by Methods 624 and 625, (November 2004) and according to the specifications in the methods. Below is a summary of the results of the data review process, followed by detailed

descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in Table 2.

SUMMARY

All samples were successfully analyzed for the target analytes according to EPA Methods 624 and 625. Method 625 samples were extracted and analyzed within the method-specified holding times, and GPC clean-up procedures were performed on all samples. Method 624 samples were prepared and analyzed within holding times. All calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory reporting limits. The QC samples, including the ongoing precision and recovery samples (OPR) and MS/MSD samples, as well as surrogate and internal standard recoveries, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

Multiple Qualifiers

Some of the analytical results were affected by multiple qualifiers. In cases where these qualifiers suggest different biases, SCC considers the data to be estimated values. The effect of each QC failure and its associated qualifier is described in the data review narrative. Where multiple qualifiers occur, the cumulative effects of the associated qualifiers are documented in the attached Table 2.

DATA ISSUES: METHOD 624

Sample Results

According to the laboratory narrative, all volatile vials for sample 65411 contained headspace upon receipt. Consequently, the results for this sample should be considered to be of acceptable quality, but they may be minimum values. Note that this sample was prepared and analyzed at a two-fold dilution due to foaming during the purging procedure. The MLs for this sample reflect the two-fold dilution.

Two of the four surrogates were recovered above the acceptance criteria in solid sample 65539. The sample was reanalyzed and had similar recoveries. In instances where some, but not all, of the surrogates exceed criteria, SCC considers the preparation process to be in control, based on the acceptable recovery of the remaining surrogates. However, other related QC results are examined to rule out the possibility of a matrix interference in the sample. For this sample, the percent recoveries for all of the internal standards were below the specified criteria. Therefore, SCC considers the detected results in sample 65539 to be estimated values. These instances are detailed in Table 2A.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples

MS/MSD samples were prepared for aqueous samples 65519 and 65527. Trichlorofluoromethane was recovered above the specified criteria in the MS prepared for sample 65519. However, since this analyte was not detected in the unspiked sample, SCC does not believe that the high recovery adversely affects the sample result.

DATA ISSUES: METHOD 625

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples

MS/MSD samples were prepared for aqueous samples 65511, 65519, and 65527. In all three MS/MSDs, the relative percent difference (RPD) between the MS and MSD exceeded the acceptance criteria for

several analytes, and the percent recovery for phenol was either above or below the acceptance criteria in the MS. When recoveries are above or below method criteria, the result for that analyte in the unspiked sample is considered to be either a maximum or minimum value, respectively. However, when combined with an RPD failure, as is the case for phenol in these samples, SCC considers detected results in the associated unspiked samples to be estimated values. Analytes not detected in the unspiked sample are not considered to be affected by the RPD failure. These instances are detailed in Table 2B.

Surrogate Recoveries

One or more surrogate recoveries were below the acceptance criteria for aqueous samples 65391, 65399, 65403, 65407, 65411, and 65499, and the recoveries for the surrogate 2,4,6-tribromophenol were below the acceptance criteria for solid samples 65543 and 65556. In sample 65459, the surrogate phenol-d_5 was recovered above the acceptance criteria, and in sample 65411, terphenyl-d_{14} was recovered above the acceptance criteria. In instances where some, but not all, of the surrogates exceed the criteria, SCC considers the extraction process to be in control based on the acceptable recovery of the remaining surrogates. However, other related QC results are examined to rule out the possibility of a matrix interference in the samples. For the aqueous samples, the percent recoveries for one or more of the internal standards were also above or below the specified criteria. In cases where both surrogate and internal standard recoveries are low, SCC considers detected results in these samples to be minimum values. In cases where the surrogates and internal standards contain both high and low recoveries, SCC considers detected results to be estimated values. These instances are detailed in Table 2B.

The surrogates were diluted out in the analysis of sample 65539 because of the dilution of the extract that was required to get the results for bis(2-ethylhexyl)phthalate within the calibration range. As a result, there are no means by which to determine whether or not the extraction procedure was in control. Therefore, SCC considers the detected results in this sample to be estimated values. These instances are detailed in Table 2B.

Ongoing Precision and Recovery (OPR)

Due to a laboratory oversight, the spiking solutions used by the laboratory for the MS/MSDs, and for four of the five OPR samples prepared for both methods contained an abbreviated list of target compounds. The unspiked sample associated with each MS/MSD is qualified as detailed above and in Table 2B. However, since all OPR percent recoveries were acceptable, including the one OPR spiked with the complete compound list, SCC believes that the laboratory performance is in control and that the sample data are not affected by the abbreviated list of target compounds.

TECHNICAL NOTES

Analysis of 1,2-, 1,3-, and 1,4-Dichlorobenzene

Due to the nature of the three dichlorobenzenes, (1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene), these compounds may be analyzed by either Method 624 or Method 625. For this episode, the laboratory reported the sample results for these analytes by both methods. All sample results were non-detects. Because Method 625 is the more common method associated with the analysis of the dichlorobenzenes and in order to maintain consistency in the analytical database, SCC has included only the sample results from Method 625 in the database.

Target Analyte List

Due to the large number of analytes that may be detected using these methods, the target compound lists for Methods 624 and 625 may vary slightly depending on the laboratory performing the analysis. For Episode 6504, the target analyte list differs from Episode 6503 in that it does not include the following analytes: benzidine, hexachlorocyclopentadiene, N-nitrosodiphenylamine, and N-nitrosodimethylamine. Note, however, that sample results for benzidine in Episode 6503 were excluded due to a QC failure.

Reporting Limits

The reporting limits requested for this project are the same limits required for Methods 1624 and 1625. For Method 624, however, the laboratory reported levels lower than those required for Method 1624. The laboratory limits for both methods, however, reflect the lowest initial calibration standard, adjusted for sample size and dilution.

Some sample results in this episode were reported by the laboratory with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit. In keeping with current EAD practices, and to maintain consistency in the database, all "J" flagged data will be reported in the database as non-detects at the MLs as specified in Method 1624 and 1625, as required for this project.

Sample Preparation - Method 625

The extracts of samples 65411 and 65455 would concentrate to only 5 mL, rather than the method-specified 1 mL. The reporting limits for these samples reflect the 5-mL extract volume.

Sample Reanalysis - Surrogate Recoveries

Sample 65499 was reextracted and reanalyzed (e.g., a new aliquot of the original sample was extracted) due to low surrogate recoveries. However, since the reextraction was performed outside of the extraction holding time, only the results from the original analysis are included in the database.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's data review team leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2A
Data Review Summary Table

Episode: 6504 **Analysis:** Method 624

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
65411	All target analytes listed in Method 624	Minimum values	Headspace observed in all vials for this sample	NA	NA
65539	toluene	Estimated value	High surrogate recoveries, low internal standard recoveries	NA	25 µg/kg
65539	ethyl benzene	Estimated value	High surrogate recoveries, low internal standard recoveries	NA	40 µg/kg

Table 2B
Data Review Summary Table

Episode: 6504 **Analysis:** Method 625

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
65511 65519	phenol	Estimated values	High MS recovery and RPD between MS and MSD exceeds criteria	NA	33 µg/L 57 µg/L
65527	phenol	Estimated value	Low MS recovery and RPD between MS and MSD exceeds criteria	NA	69 µg/L
65459	diethyl phthalate	Maximum value	High internal standard results and high surrogate recovery	NA	16 µg/L
65391	phenol	Minimum value	Low internal standard results and low surrogate recoveries	NA	58 µg/L
65399 65403 65407 65411 65499	phenol	Estimated values	High internal standard results and low surrogate recoveries	NA	35 µg/L 39 µg/L 43 µg/L 100 µg/L 32 µg/L
65539	bis(2-ethylhexyl) phthalate	Estimated value	Surrogates diluted out	NA	130,000 µg/kg

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MEMORANDUM

DATE: January 27, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist
Sample Control Center

PC

SUBJECT: Data Review Narrative for PCB Congener Analyses for the Alaskan Cruise Ship Industry, Episode 6504

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of chlorinated biphenyl congeners by EPA Method 1668A for one sample in Episode 6504. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6504	65455	Aqueous	SP5, Influent Wastewater	8/09/04	1668A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Chlorinated Biphenyl Analysis (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with this sample. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

The sample was successfully extracted and analyzed for the target analytes in EPA Method 1668A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks associated with this sample detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance was acceptable, with the clarification provided below.

Reporting Limits

The laboratory's reporting limits are at the method-specified minimum levels (MLs). The sample was extracted using a 795-mL aliquot, rather than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the MLs for sample 65455 by 26%. The MLs provided in the database for this sample reflect the smaller sample volume.

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If you have any questions regarding the analyses of this sample or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

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MEMORANDUM

DATE: January 27, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Pesticide Analyses for the Alaskan Cruise Ship Industry
Episode 6504

OVERVIEW

Under EPA Purchase Order EP-C-04-046, Pacific Analytical, Inc. (PAI) submitted data for the analysis of organohalide pesticides by EPA Method 1656A and organophosphorus pesticides by EPA Method 1657A for two samples in Episode 6504. Table 1 provides a list of samples, matrices, descriptions, sampling dates, and the required analytical methods.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Method
65395	Aqueous	SP1, Galley wastewater	8/10/04	1656A, 1657A
65459	Aqueous	SP5, Influent to wastewater	8/10/04	1656A, 1657A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Pesticide Analyses (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary tables (Tables 2A and 2B).

SUMMARY

All samples were successfully extracted and analyzed for the target analytes in EPA Methods 1656A and 1657A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits. All organohalide pesticides samples were processed through gel permeation chromatography (GPC), Florisil, and sulfur removal cleanups. All organophosphorus pesticides samples were processed through GPC and carbon column cleanup. The QC samples, including the ongoing precision and recovery sample (OPR) demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below. No matrix spike/matrix spike duplicate (MS/MSD) samples were required for this episode.

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Reporting Limits

The laboratory's reporting limits are based on the lowest calibration points specified in the methods, adjusted for dilution, rather than the minimum levels (MLs) listed in the methods. In most cases, the laboratory's reporting limits are lower than the method-specified MLs.

Some sample results in this episode were reported by the laboratory with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit. In keeping with current EAD practices, and to maintain consistency, all "J" flagged data will be reported in the database as non-detects at the laboratory's reporting limits.

DATA ISSUES: METHOD 1656A

Preparation Blank

Kepone was detected in the preparation blank associated with the samples at 0.617 µg/L, which was below the laboratory's reporting limit. Since the sample results are less than five times the blank result, there are no means by which to ascertain whether or not the presence of the analyte may be attributed to contamination. Considering the fact that kepone has not been manufactured or registered for use in the U.S. for many years, it seems unlikely that the peak tentatively identified as kepone during this analysis is actually kepone. After consultation with SCC, EPA decided that high resolution GC/MS confirmation of this sample was not warranted. Therefore, SCC recommends that the kepone results of 1.81 µg/L and 1.46 µg/L in samples 65395 and 65459, respectively, be reported in the database as non-detects at the laboratory's reporting limit. See Table 2A.

Ongoing Precision and Recovery (OPR)

Metribuzin, norflurazon, and carbophenothion were recovered below the method-specified criteria in the OPRs associated with the samples in this episode. Therefore, SCC considers the non-detects in these samples to be of acceptable quality, but they may be minimum values. See Table 2A.

Surrogate Recoveries

For all samples in this episode, the surrogate recoveries for decachlorobiphenyl on both columns are below the method-specified criteria. However, the other two surrogate recoveries are within the method-specified criteria, indicating that the extraction efficiency was in control. Therefore, SCC believes that the data quality for these samples is not affected by the low recovery of one surrogate. None of the organohalide pesticides were detected in any samples in this episode.

DATA ISSUES: METHOD 1657A

Ongoing Precision and Recovery (OPR)

Methamidophos was not recovered in any of the OPRs associated with the samples in this episode. This analyte was not detected in either sample in this episode. Because it cannot be ascertained whether or not this analyte would have been detected if present in the samples, SCC recommends excluding methamidophos results from the database. See Table 2B.

Surrogate Recoveries

For sample 65395, the surrogate recoveries for triphenylphosphate on both columns are below the method-specified criteria. However, the other surrogate recovery is within the method-specified criteria indicating that the extraction efficiency was in control. Therefore, SCC believes that the data quality for this sample is not affected by the low recovery. None of the organophosphorus pesticides were detected in any samples in this episode.

If you have any questions regarding the analyses of these samples or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2A
Data Review Summary Table

Episode: 6504 **Analysis:** 1656A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65395, 65459	kepone	Report in the database as non-detects	Sample results < 5x blank result	NA	ND
65395, 65459	metribuzin, norflurazon, carbophenothion	Acceptable quality, but may be minimum value	Low OPR recoveries	NA	ND

Table 2B
Data Review Summary Table

Episode: 6504 **Analysis:** 1657A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65395, 65459	methamidophos	Exclude non-detects from database	No OPR recoveries	Exclude	NA

ND = Non-detect at the laboratory's reporting limit. See level in database
NA = Not applicable

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6504

Data Validation Report For Settleable Solids Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

December 16, 2004

Settleable Solids Method 160.5

Completeness

During Sampling Episode 6504, a total of 30 samples (excluding QC samples) were collected for analysis of settleable solids (SS) by EPA Method 160.5. All samples received by the laboratory were analyzed for SS for a completeness of 100% (all planned samples were collected and analyzed). Sample numbers for SS are provided in Table 1.

Table 1. SS Samples Collected During Sampling Episode 6504

Sample Numbers	Sample Point Description
65455, 65459, 65463, 65467, 65471	Treatment System Influent
65495, 65499, 65503, 65507, 65511, 65519, 65523, 65535	Treatment System Effluent
65415, 65419, 65423, 65427, 65431	Accommodations
65391, 65395, 65399, 65403, 65407	Galley
65435, 65439, 65443, 65447,65451	Laundry
65411	Food Pulper
65547	Source Water

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete SS data for the samples listed in Table 1.

Holding Times

Method 160.5 requires SS samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates all SS samples received by the laboratory were analyzed within the 48 hour holding time.

Precision Analysis

Reproducibility for SS is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking targets the RPD for all field duplicate samples as less than 30%. Field duplicate samples were collected for SS, and the results are shown in Table 2. The RPDs shown in Table 2 could not be calculated because all duplicate sample results were less than the laboratory reported detection limit. Although the RPD for these samples cannot be calculated, SS analysis precision is acceptable for this program, and the reported SS results are valid.

Table 2. Relative Percent Difference Between Field Duplicate Samples

Sample No.	SS Result	Sample No.	SS Result	RPD	RPD Target
65495	<0.11 ml/L	65519	<0.12 ml/L	NA	<30%
65499	<0.11 ml/L	65523	<0.11 ml/L	NA	<30%
65511	<0.10 ml/L	65535	<0.10 ml/L	NA	<30%

NA: RPD cannot be calculated since one or both of the sample results is less than the detection limit.
RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004

Data Quality Assessment

This data validation assessment indicates the SS data collected during Sampling Episode 6504 can be used for the large cruise ship rulemaking effort.

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MEMORANDUM

DATE: February 15, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: **Revised** Data Review Narrative for Available Cyanide Analyses by Method OIA-1677 for the Alaskan Cruise Ship Industry, Episode 6504

OVERVIEW

*The January 18th version of this narrative was revised to correct the sampling date for sample 65407 in Table 1. The change is shown in **bold**.*

Under EPA Purchase Order EP-C-04-060, Bayer Material Science LLC, submitted available cyanide data by EPA Method OIA-1677 for 31 samples in Episode 6504. Table 1 provides a list of the samples, matrices, and descriptions. Available cyanide was the only analysis performed by Bayer for these samples.

Table 1 - Sample Identifiers, Descriptions, and Sampling Date

EPA Sample #	Matrix	Sample Description	Sampling Date
65391	Aqueous	SP1, Galley wastewater	8/09/04
65395	Aqueous	SP1, Galley wastewater	8/10/04
65399	Aqueous	SP1, Galley wastewater	8/11/04
65403	Aqueous	SP1, Galley wastewater	8/12/04
65407	Aqueous	SP1, Galley wastewater	**8/13/04**
65411	Aqueous	SP2, Food pulper	8/11/04
65415	Aqueous	SP3, Accommodations wastewater	8/09/04
65419	Aqueous	SP3, Accommodations wastewater	8/10/04
65423	Aqueous	SP3, Accommodations wastewater	8/11/04
65427	Aqueous	SP3, Accommodations wastewater	8/12/04
65431	Aqueous	SP3, Accommodations wastewater	8/13/04
65435	Aqueous	SP4, Laundry wastewater	8/09/04
65439	Aqueous	SP4, Laundry wastewater	8/10/04
65443	Aqueous	SP4, Laundry wastewater	8/11/04
65447	Aqueous	SP4, Laundry wastewater	8/12/04
65451	Aqueous	SP4, Laundry wastewater	8/13/04
65455	Aqueous	SP5, Influent to wastewater treatment	8/09/04

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Table 1 - Sample Identifiers, Descriptions, and Sampling Date

EPA Sample #	Matrix	Sample Description	Sampling Date
65459	Aqueous	SP5, Influent to wastewater treatment	8/10/04
65463	Aqueous	SP5, Influent to wastewater treatment	8/11/04
65467	Aqueous	SP5, Influent to wastewater treatment	8/12/04
65471	Aqueous	SP5, Influent to wastewater treatment	8/13/04
65495	Aqueous	SP7, Effluent from wastewater treatment	8/09/04
65499	Aqueous	SP7, Effluent from wastewater treatment	8/10/04
65503	Aqueous	SP7, Effluent from wastewater treatment	8/11/04
65507	Aqueous	SP7, Effluent from wastewater treatment	8/12/04
65511	Aqueous	SP7, Effluent from wastewater treatment	8/13/04
65519	Aqueous	SP8, Effluent from wastewater treatment	8/09/04
65523	Aqueous	SP8, Effluent from wastewater treatment	8/10/04
65527	Aqueous	SP8, Effluent from wastewater treatment	8/11/04
65539	Solid	SP9, Biosludge	8/09/04
65547	Aqueous	SP11, Source water	8/12/04

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), and with the specifications listed in the analytical requirements summary for this episode. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the method-specified holding times for available cyanide. Initial precision and recovery samples (IPRs) were successfully performed prior to sample analysis. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks were performed and there was no contamination detected above the laboratory reporting limits. The QC samples, including the ongoing and precision recovery sample (OPR) and matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable, with the exception of the data issues described below.

DATA ISSUES

Available Cyanide Greater than Total Cyanide

A comparison of the total cyanide results and available cyanide results for samples 65395, 65455, 65459, 65463, 65467, and 65471 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at approximately 11 to 36 µg/L. In addition, total cyanide was reported as present in sample 65411 at 6 µg/L, while the available cyanide result was 35.7 µg/L (e.g., six time the total cyanide result).

Sample 65395 is listed as the galley wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Therefore, lacking matrix-

specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65395 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65411 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system, and as noted above, there are no MS/MSD data that demonstrate method performance for matrices other than effluents. During the review of the data, SCC noted that the traffic report for the aliquot of Sample 65411 for total cyanide analysis indicated that the aliquot was collected at 14:00 on 8/10/04, while the traffic report for the aliquot submitted for available cyanide analysis indicated that that aliquot was collected at 3:00 PM (15:00) on 8/11/04. This concern was resolved following discussions with EPA and the sampling contractor, whose field records indicated that both aliquots were collected at the same time, and that the one traffic report was incorrect. Having resolved the issue of the time of sample collection, but lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65411 in the database, but flagging them to indicate the irreconcilable differences.

Samples 65455, 65459, 65463, 65467, and 65471 are all influents to treatment, collected from the same sampling point on consecutive days. The results from samples 65463, 65467, and 65471 are remarkably consistent, varying by only 0.2 μg/L across all three samples. The results for samples 65455 and 65459 are similar to one another, but about twice the concentrations found in the other three samples from this sampling point. There are no MS/MSD analyses that demonstrate method performance for this matrix type, but the consistency in the results suggests that whatever matrix effects may be taking place, they are reproducible. However, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65455, 65459, 65463, 65467, and 65471 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6504, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Please note that the samples were analyzed for total cyanide by ProChem (formerly QBioChem). A separate data narrative has been prepared for the total cyanide analysis.

Biosludge Sample Result

Sample 65539 was a dried biosolid sample. Method OIA-1677 is designed for the analysis of aqueous samples. In order to analyze the biosolids sample, Bayer received permission from the Sample Control Center to modify the method to perform an alkaline leaching of the biosolids and then analyze the leachate for available cyanide. As part of their demonstration of the effectiveness of the method modifications for biosolids, MS/MSD samples were prepared for biosludge sample 65539. The spike recoveries from the MS/MSD were 3.5 and 4.5%, well below the laboratory's's expectations for the modified procedures. Therefore, the laboratory prepared a second set of MS/MSD samples, using mercuric cyanide to spike the samples, and a third MS/MSD set using potassium cyanide, in an effort to determine if the form of cyanide had an effect on method performance. The spike recoveries for the mercuric cyanide were 3.5 and 3.6%, and the recoveries for the potassium cyanide samples were 2.6 and 2.8%.

Based on these results, the laboratory concluded that the modified method may not be suitable for the determination of available cyanide in dried biosludge, or that the cyanide may have reacted with the biosludge sample so that the cyanide is no longer "available." SCC concurs with the laboratory's assessment of the performance of the method modifications relative to this biosolid sample. Therefore,

SCC considers the non-detect available cyanide data in sample 65539 to be invalid and recommends excluding it from the database. This case is detailed in Table 2.

TECHNICAL NOTES

Reporting Limits

The laboratory reported sample results down to the method detection limit (MDL), rather than the method-specified minimum level (ML). In keeping with current SCC practices, and in order to maintain consistency in the database, the reporting limits for available cyanide have been adjusted in the database to reflect the method-specified ML of 2.0 µg/L.

If you have any questions regarding the analyses of these samples or the review of these data, please contact me by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6504 **Analysis:** Available Cyanide

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65395, 65411, 65455, 65459, 65463, 65467, 65471	Available cyanide	Irreconcilable results for total and available cyanide	Results for available cyanide greater than total cyanide	IRR	NA
65539	Available cyanide	Exclude from database	MS/MSD data suggest that result may be invalid for biosludge	Exclude	NA

NA = Not applicable
IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.

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MEMORANDUM

DATE: March 22, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty
Senior Scientist

SUBJECT: Further Examination of Ammonia Data for Episodes 6503 to 6506

At EPA's request, SCC performed additional reviews of the ammonia data for Episodes 6503 through 6506 for the Alaskan Cruise Ship project. The root of EPA's concern is an apparent discrepancy between the ammonia results for samples in Episodes 6503 and 6505 versus the results for samples from similar sampling points in Episodes 6504 and 6506.

SCC re-examined the results and raw data submitted by ALSI for Episodes 6503 and 6505 and the results and raw data submitted by ProChem for Episodes 6504 and 6506. SCC staff re-examined all of the sample shipping and custody records, looking for any discrepancies. SCC staff also contacted both laboratories and asked about potential problems with the ammonia analyses for these samples.

The results of this investigation confirm our original data review results, namely, there are no manifest errors in the data. The quality control (QC) results from each laboratory support the results provided and do not suggest any pervasive problems with the analyses (i.e., matrix spike recoveries and OPR results were well within the acceptance limits, blanks were free of ammonia at the levels of interest).

Both laboratories used the distillation procedure in EPA Method 350.2 to prepare the samples for the determinative analysis. Method 350.2 discusses the use of "microdistillation" glassware in place of the larger glassware in the method. Both laboratories employed microdistillation glassware, with ALSI using a 150-mL initial sample volume and ProChem using a 100-mL volume.

The laboratories used different determinative methods for ammonia. ALSI used EPA Method 350.1, an automated colorimetric method, whereas ProChem used EPA Method 350.3, an ion selective electrode procedure. Both methods are approved for ammonia analysis at 40 CFR 136. Method 350.1 has a much narrower dynamic range than Method 350.3 (0.01 to 2 mg/L versus 0.05 to 1400 mg/L). As a result, ALSI had to analyze many of the samples at dilutions of 10 - 100x, while ProChem did not have to dilute many of the samples. SCC examined the blank data from both laboratories and there is no evidence that the reagent water used to prepare blanks and to dilute samples would have contributed to the sample results for ammonia. SCC reviewed the reporting limits used by both laboratories relative to the capabilities of the methods. As noted above, the dynamic range of Method 350.1 is five times lower than that of Method 350.3, however the samples from this project were generally not at such low levels. Therefore, there is no evidence that method sensitivity or reporting practices resulted in the discrepancies of concern to EPA.

It is important to note that the two laboratories never analyzed aliquots of the same samples, so there is no direct means of comparing their results.

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In summary, SCC's examination of the data did not provide any explanation for the differences in the results for ammonia from these two laboratories. Although the laboratories used different methods for the determinative analyses, both methods are approved at 40 CFR 136 and both methods are applicable to the samples for this project. This review was limited to the analytical data provided by the laboratories and SCC cannot rule out the possibility that differences in sampling, sample handling prior to arrival at the laboratories, or in the waste collection and treatment systems among the cruise ships affected the samples analyzed by the two laboratories.

If you have any questions about the information in this memorandum or the ammonia results in the database, please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com.

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MEMORANDUM

DATE: January 18, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty
Senior Scientist

SUBJECT: Issues Associated with Results for Total Cyanide versus Available Cyanide for Episodes 6503, 6504, 6505, and 6506

The purpose of this memorandum is to provide a general discussion of the analysis of various forms of cyanide in aqueous samples, describe the cyanide analyses conducted as part of EPA's investigation of discharges from Alaskan cruise ships, and provide recommendations regarding specific results from Sampling Episodes 6503, 6504, 6505, and 6506.

Forms of Cyanide

Cyanide is an inorganic moiety composed of one carbon atom and one nitrogen atom that is most often found as an anion with a charge of -1. The cyanide anion can bond with various metals or other elements to form a wide range of cyanide compounds. The simplest form of cyanide is hydrogen cyanide, HCN, which readily dissociates into H^+ and CN^- in water. HCN is known as "free cyanide" and is the most toxic form of cyanide. Most forms of cyanide are toxic, with their toxicities depending on their ability to release free cyanide.

"Total cyanide" (or "cyanide, total") is an operationally defined term used to describe the cyanides that are measured using the total cyanide test. Total cyanide methods attempt to measure the amount of CN^- present in a sample, regardless of its oxidation state or complexation to other ions or compounds. Some complexes and organic cyanide compounds are resistant to the dissociation that occurs during the digestion/distillation step, and others are completely decomposed. Therefore, total cyanide is a method-defined parameter because the analytical conditions determine the actual analyte quantity measured.

Compounds such as metallocyanides are resistant to oxidation, with iron cyanide being one of the most resistant, and nickel, copper, and noble metal cyanides being somewhat resistant. These compounds will contribute to the measured total cyanide to some degree, but are not always completely recovered by the digestion/distillation procedure. Cyanide compounds such as thiocyanate, cobaltocyanide compounds, and cyanohydrin organic compounds are not measured at all by this procedure include because they decompose during the digestion procedure.

Two other operationally defined groups of cyanide species are "available cyanide," and "cyanide amenable to chlorination" (or "amenable cyanide"). Available cyanide generally encompasses both the free cyanide and those complexed species that are relatively easily dissociated in a weak acid solution. Amenable cyanide is the term used to describe that fraction of cyanide that can be destroyed by the common wastewater treatment procedure of chlorinating the wastewater. Some cyanides in solution will react with chlorine (Cl_2) to form cyanogen chloride (CNCl), a highly toxic gas with limited solubility. The cyanogen chloride hydrolyzes at alkaline pH to form the cyanate ion (CNO^-), which is much less toxic than the parent cyanide. Amenable cyanide encompasses the true free cyanide portion, plus additional cyanides that easily dissociate in aqueous solutions.

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Analytical Methods for the Analysis of Cyanide in Aqueous Samples

Total Cyanide Methods

The seven methods approved at 40 CFR 136 for total cyanide in aqueous samples are:

- EPA Method 335.2
- EPA Method 335.3
- Standard Method 4500-CN^- D
- Standard Method 4500-CN^- E
- ASTM Method D2036-98A
- USGS Method I-3300-85
- USGS Method I-4302-85

EPA Methods 335.2 and 335.3 were employed by the two laboratories that analyzed samples from Episodes 6503, 6504, 6505, and 6506 for total cyanide. However, this general discussion applies to all seven approved methods.

All of the total cyanide methods involve digestion of the sample using concentrated sulfuric acid with magnesium ion in solution as a catalyst. (The digestion procedure is presented as the stand-alone procedure Standard Method 4500-CN^- C). The cyanide is converted to HCN gas, which is collected in a scrubber containing NaOH. This solution is then analyzed for the CN^- ion. The determinative methods use one of several techniques to measure CN^-, including titration with silver nitrate, colorimetry with an organic dye, or automated distillation-colorimetry for continuous flow analytical systems that utilizes UV oxidation of the sample to release bound cyanide.

Available Cyanide Methods

The four methods approved at 40 CFR 136 for available cyanide in aqueous samples are:

- EPA Method 335.1
- Standard Method 4500-CN^- G
- ASTM Method D2036-98B
- Method OIA-1677

Method OIA-1667 was employed for the analyses of available cyanide in Episodes 6503, 6504, 6505, and 6506. However, this general discussion applies to all four approved methods.

Although these four methods are approved at 40 CFR 136 for “available cyanide,” there are slight differences in forms of cyanide that are targeted by these methods. Generally speaking, the differences are not significant in compliance monitoring, but may be more important in other types of investigations.

The OIA-1677 procedure targets the weak acid dissociable cyanide by treating the sample with ligand-exchange reagents that release cyanide ions from the metal-cyano complexes. During the analysis, cyanide ions are converted to hydrogen cyanide (HCN) that passes through a gas diffusion membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically, using a silver electrode.

EPA Method 335.1, SM 4500-CN^- G, and ASTM D2036-98B measure the cyanide amenable to chlorination. In these methods, two aliquots of the sample are analyzed. One aliquot is subjected to chlorination and the other aliquot is not. Both aliquots are distilled and analyzed for CN^-. The amenable

cyanide is calculated as the difference between the cyanide results from the chlorinated and nonchlorinated aliquots.

Difficulties and Interferences in the Analysis of Cyanide

A number of interferences affect cyanide determinations. Strong oxidizers, such as free chlorine, will destroy the "amenable" portion of cyanide. Sulfide present in the sample will oxidize cyanide into thiocyanate, which is not measurable in the cyanide methods. The sample should be tested for sulfide at the time of sample collection, and if sulfides are found, they should be removed by precipitation with lead carbonate or cadmium nitrate. This precipitation procedure should take place before the sample is preserved with NaOH, and any insoluble sulfide that is produced should be removed by filtration. Additional steps may be needed if the sample contains sulfide *and* particulate matter that may consist of alkali metal-heavy metal-cyanide complexes.

Most interferences in the total cyanide determination are removed by the distillation step, but some are not. Nitrate and nitrite can form cyanide as a reduction product of nitrogen-containing organic compounds, and are removed by the addition of sulfamic acid during distillation. Aldehydes can form cyanohydrins, which will convert to nitrile during the digestion. Sulfides also can be produced during distillation, and will distill along with cyanide and form thiocyanate. Sulfide production can be prevented by the addition of lead carbonate to the absorber solution, and the subsequent filtration of the absorber solution before analysis. Other potential interferences include sugars that can form cyanohydrins, sulfur compounds that may release sulfide, compounds that could release or form nitrite, as well as any sample constituent that could produce one of the interferences under the conditions of the digestion.

Method OIA-1677 does not employ a digestion step. Therefore, sulfides must be removed by the precipitation procedure described above. In addition to concerns about sulfides reacting with the cyanide in the sample before it can be measured (i.e., a negative interference), sulfides also can be a positive interference in this procedure if they react with acid in the sample to produce hydrogen sulfide (HS_2). The hydrogen sulfide will cross the membrane in the gas diffusion cell and produce a signal at the silver electrode that would be measured as cyanide. As noted in the method, "polysulfides" (compounds containing more than one sulfide) can be intractable interferences.

Interpretation of Cyanide Results

In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. While this usually holds true for wastewater effluent samples, some effluents and some other sample types, such as influents, may yield results in which the free or available cyanide results exceed the total cyanide results. For example, the results for free cyanide derived using the chlorination technique can result in free cyanide concentrations greatly in excess of total cyanide concentrations. When this occurs, it is likely due to the formation of cyanide by chlorination of nitrogen-containing organic compounds in the sample. While it might be possible to determine if such nitrogen-containing organics were present in the sample, this step is neither required nor practical for laboratories performing routine cyanide analyses.

Sulfides that may be in the sample present a significant possibility for false negative results for total cyanide through the oxidization of cyanide to thiocyanate, which is not measured by the cyanide methods, as discussed above. Sulfides can be both a negative interference and a positive interference with the determination of available cyanide by Method OIA-1677, as described above.

It is also important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the amenable cyanide determination is made using

separate aliquots of a separate sample. Thus, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results.

While the results for any cyanide measurement are evaluated by SCC relative to the requirements of the methods used for the determinations, it may not be possible to identify problems that would invalidate one cyanide fraction or the other. In instances where there are one or more QC failures associated with one of the cyanide fractions, but not with the other fraction, the results for the fraction with the QC failures will be appropriately qualified.

In instances where there are no QC failures associated with either cyanide fraction, but the available cyanide results are greater than the total cyanide results by a large margin, there is no way to determine which analysis was correct. In such cases, both sets of cyanide results are suspect. For the purposes of reviewing results for EPA's Effluent Guidelines Program, when cyanide is reported as present (e.g., not a non-detect) in both fractions and there are no QC failures in either fraction, differences where the available cyanide results are more than 30% above the total cyanide results suggest that irreconcilable problems exist. The 30% difference is a consensus value used by SCC. Differences less than 30% are considered a function of the routine variability that could be present in both measurements.

When such irreconcilable problems exist with the results of paired samples analyzed for both total and available cyanide, SCC recommends that both results (total and available) be included in the database, and that both results be flagged to alert the data user to the presence of such problems.

Cyanide Methods Used for Samples from the Alaskan Cruise Ship Project

The following table lists the methods used for total and available cyanide for Episodes 6503, 6504, 6505, and 6506. Two different laboratories performed the total cyanide analyses for these four episodes, using two different methods approved at 40 CFR 136. One other laboratory analyzed the available cyanide for all four episodes using Method OIA-1677.

Episode #	Method for Total Cyanide	Method for Available Cyanide
6503	EPA Method 335.3	Method OIA-1677
6504	EPA Method 335.2	Method OIA-1677
6505	EPA Method 335.3	Method OIA-1677
6506	EPA Method 335.2	Method OIA-1677

Based on communications with the sampling contractor, the samples were tested for sulfide in the field, using a field colorimeter with a detection limit of approximately 10 µg/L. Samples testing positive for sulfides were treated in the field to minimize the interferences. Because of concerns regarding whether the treated samples were subsequently filtered in the field, the laboratories were instructed to filter any sample showing turbidity.

A review of the traffic reports (TRs) for the samples in these four episodes indicates that some of the samples in Episode 6503, the first episode in the Alaskan Cruise Ship project, were not treated with lead carbonate to remove sulfides. SCC consulted EPA and the sampling contractor and determined that the following 11 samples were not treated with lead carbonate:

65202, 65207, 65211, 65227, 65231, 65235, 65269, 65273, 65277, 65283, and 65295

In an effort to address the potential positive interference of nitrate and nitrite in the samples, the laboratories performing the total cyanide analyses were advised to increase the amount of sulfamic acid added to each sample during distillation by a factor of 2, from 2 g per sample to 4 g per sample.

Episode-specific Findings

SCC has reviewed the results for both total cyanide and available cyanide in Episodes 6503, 6504, 6505, and 6506. Episode-specific findings are detailed below.

In addition to the data qualifiers described in SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), two additional qualifiers were developed to address the total and available cyanide results from the Alaskan Cruise Ship Project. In cases where the available cyanide results exceed those for total cyanide by more than 30% and there are not any matrix-specific quality control data such as matrix spike recoveries, the total cyanide and available cyanide results will be flagged with the "IRR" qualifier. The "SCC Reason" field in the database for such results will read "Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose."

In other instances, when SCC's review identifies multiple concerns with the results for a given sample, including those that begin with sample collection and others involving the analysis of the sample itself or any associated quality control samples, the total cyanide and available cyanide results will be flagged with the "MISCA" qualifier. The "SCC Reason" field in the database for such results will read "Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample."

Episode 6503

Three sets of matrix spike/matrix spike duplicate (MS/MSD) samples were prepared for total cyanide analysis in Episode 6503 on samples 65207 (accommodations wastewater), 65269 (an effluent), and 65273 (an effluent). The MS/MSD recoveries for the three aqueous MS/MSD pairs were below the acceptance limits:

- 22% and 21% for sample 65207,
- 30% and 33% for sample 65269, and
- 5% and 1% for sample 65273

suggesting a potential for low bias in the total cyanide results for the associated aqueous samples.

The recoveries for the laboratory control samples (LCS, OPR, or QC check sample) analyzed along with the field samples were acceptable, indicating that the laboratory's overall analytical process was in control and suggesting either problems with the distillation process or an interference present in the sample matrix. Because the focus of the EAD analytical contracts is on effluent samples and because there are no acceptance criteria for aqueous matrices other than effluents, no MS/MSD analyses were performed on samples representing influents to the treatment process.

The total cyanide result for Sample 65273 (effluent) was reported as a non-detect at 5 µg/L and available cyanide was a non-detect at 2 µg/L. An MS/MSD pair for available cyanide was prepared from this sample and had recoveries of 101% and 102% respectively, while the MS/MSD recoveries for total cyanide were 5% and 1%, as noted earlier. This suggests a significant potential for low bias in the total cyanide result. Therefore, based on the low MS/MSD recoveries for total cyanide in this sample, the total

cyanide non-detect is considered a minimum value and the available cyanide result is considered acceptable without qualification.

There were nine other samples in Episode 6503 that exhibited the pattern of total cyanide results less than the available cyanide results. Samples 65219, 65227, 65231, and 65235 are influents to treatment and, as noted above, there are no MS/MSD analyses that demonstrate the performance of either method for this matrix type. Samples 65227, 65231, and 65235 also are among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and given the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for samples 65227, 65231, and 65235 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples. Sample 65219 was treated in the field, therefore SCC recommends including both cyanide results for sample 65219 in the database, but flagging them to indicate the irreconcilable differences.

The total cyanide results for Sample 65207 (accommodations wastewater) were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 15.7 µg/L. The MS/MSD recoveries for total cyanide were 21% and 22%, as noted earlier. Sample 65207 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, given the low MS/MSD recoveries for total cyanide in this sample and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65207 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65211 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Total cyanide was detected at 14 µg/L, while available cyanide was reported at 88.4 µg/L. Sample 65211 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65211 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65295 is listed as a source water sample, a matrix type that should not present significant analytical difficulties. Sulfide was not detected in this sample by the field test performed at the time of collection and therefore, this sample is among the 11 samples that were not treated with lead carbonate. Although the presence of available cyanide at 19 µg/L in the source water is unexpected, there is no analytical evidence to suggest that the available cyanide result be excluded. However, an engineering review or other information not available to SCC may lead to a different conclusion. Therefore, SCC recommends including both cyanide results for sample 65295 in the database, but flagging them to indicate the irreconcilable differences.

Episode 6503 included two sets of field duplicate samples that were sent to the laboratories blind. The two pairs were samples 65261 and 65281, and samples 65265 and 65283, all effluent samples. The total cyanide results in sample 65261 were reported as a non-detect at 5 µg/L, while available cyanide was reported as a non-detect at 2 µg/L. For sample 65281, the blind field duplicate, the total cyanide results were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 8.96 µg/L. A similar pattern occurs for the cyanide results in the other field duplicate pair. Total cyanide was reported as a non-detect at 5 µg/L in both samples 65265 and 65283, while available cyanide was detected at 5.86 µg/L in sample 65265 and as a non-detect a 2 µg/L in sample 65283.

The MS/MSD recoveries for total cyanide in effluent sample 65273 were very low (1% and 5%), and low (33% and 30%) in sample 65269, suggesting a potential negative basis that may affect the total cyanide results in samples 65261, 65281, 65265, and 65283. Therefore, SCC recommends that the total cyanide results in sample 65261 and 65281 be considered minimum values. The difference between the available cyanide results in the two field duplicate samples (e.g., a non-detect at 2 µg/L and a detect at 8.96 µg/L) cannot be explained on the basis of the MS/MSD results for available cyanide in sample 65273, which was also an effluent. Given the discrepancy between the field duplicate results for available cyanide, SCC recommends including the available cyanide results for samples 65261 and 65281 in the database, but flagging them to indicate the irreconcilable differences. SCC recommends that the total cyanide results for samples 65261 and 65281 also be flagged to indicate the irreconcilable differences, as a further precaution.

Because of the low MS/MSD recoveries in the other effluent samples, the total cyanide result for sample 65265 is considered a minimum value. The available cyanide result of 5.86 µg/L is well within 30% of the reported detection limit for total cyanide (e.g., 5 µg/L), and therefore would normally not be qualified. However, because the available cyanide result in the field duplicate of the sample, 65283 is a non-detect at 2 µg/L, SCC recommends including both the total and available cyanide results for sample 65265 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65283 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Given the very low MS/MSD recoveries for total cyanide in effluent samples in this episode, SCC recommends flagging both cyanide results for sample 65283 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples.

Episode 6504

Three sets of MS/MSD samples were prepared for total cyanide analysis in Episode 6504 on samples 65519 (an effluent), 65523 (an effluent), and 65527 (accommodations wastewater), and all showed acceptable spike recoveries. Thus, there do not appear to be pervasive problems with the recovery of total cyanide in samples from this episode.

A comparison of the total cyanide results and available cyanide results for samples 65395, 65455, 65459, 65463, 65467, and 65471 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at approximately 11 to 36 µg/L. In addition, total cyanide was reported as present in sample 65411 at 6 µg/L, while the available cyanide result was 35.7 µg/L (e.g., six time the total cyanide result).

Sample 65395 is listed as the galley wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65395 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65411 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system, and as noted above, there are no MS/MSD data that demonstrate method performance for matrices other than effluents. During the review of the data, SCC noted that the traffic report for the aliquot of Sample 65411 for total cyanide analysis indicated that the aliquot was collected at 14:00 on 8/10/04, while the traffic report for the aliquot submitted for available cyanide analysis indicated that that aliquot was collected at 3:00 PM (15:00) on 8/11/04. This concern was resolved following discussions with EPA and the sampling contractor, whose field records indicated that both aliquots were collected at the same time, and that the

one traffic report was incorrect. Having resolved the issue of the time of sample collection, but lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65411 in the database, but flagging them to indicate the irreconcilable differences.

Samples 65455, 65459, 65463, 65467, and 65471 are all influents to treatment, collected from the same sampling point on consecutive days. The results from samples 65463, 65467, and 65471 are remarkably consistent, varying by only 0.2 µg/L across all three samples. The results for samples 65455 and 65459 are similar to one another, but about twice the concentrations found in the other three samples from this sampling point. There are no MS/MSD analyses that demonstrate method performance for this matrix type, but the consistency in the results suggests that whatever matrix effects may be taking place, they are reproducible. However, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65455, 65459, 65463, 65467, and 65471 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6504, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6505

The data for total cyanide samples in Episode 6505 were delivered in five separate data packages, each with its own associated QC sample results. Six pairs of MS/MSD samples were prepared for total cyanide analyses in Episode 6505 on samples 65603 (galley wastewater), 65635 (accommodations wastewater), 65711 (an effluent), 65715 (an effluent), 65719 (an effluent), and 65741 (screening solids).

The data for a seventh pair of MS/MSD samples were delivered in the data package with the results for samples 65731 (galley wastewater) and 65745 (biosolids). However, because of limitations on the sample volume that was provided to the laboratory, the MS/MSD samples were prepared from a non-EPA sample of indeterminate origin and therefore are not useful in evaluating the performance of the total cyanide method on cruise ship samples.

Three of the MS/MSD pairs for aqueous samples and the one MS/MSD pair for the solid samples had acceptable recoveries of total cyanide. None of the samples used to prepare MS/MSD aliquots were samples where the available cyanide results exceeded the total cyanide results.

The MS/MSD results for sample 65603 (galley wastewater) showed recoveries of 59% in both aliquots, which is below the acceptance limits, and suggests a potential low bias in the total cyanide result for that sample. The available cyanide result of 2.2 µg/L is below the detection limit for the total cyanide analysis. Therefore, SCC recommends qualifying the total cyanide result as a minimum value and accepting the available cyanide result as reported.

Although MS/MSD samples were prepared from sample 65741 (screening solids) and met the acceptance criteria, there are no MS/MSD results for the biosolids matrix in this episode. This limits SCC's ability to evaluate the potential effects of the sample matrix for sample 65745 (biosolids), where the available cyanide results are almost 40% higher than the total cyanide results. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65745 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65731 is a galley wastewater. The only MS/MSD results for galley wastewater in this episode are for sample 65603, where the recoveries were below the acceptance criteria. Given the

potential for low bias in this matrix, SCC recommends qualifying the total cyanide result as a minimum value. SCC recommends including both cyanide results for sample 65731 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65659 is an influent sample and MS/MSD aliquots are not prepared for influents, as discussed earlier. Total cyanide was reported as not detected and the available cyanide was reported at 6 times the total cyanide detection limit. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65659 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6505, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6506

A comparison of the total cyanide results and available cyanide results for samples 65896, 65900, 65904, 65908, and 65912 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at levels from approximately 36 to 77 µg/L.

All five of these samples are from the same sampling point, SP 2, and represent influents to the black water and gray water treatment system. Thus, these samples are not treated effluents. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65896, 65900, 65904, 65908, and 65912 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6506, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Summary of Results from Episodes 6503, 6504, 6505, and 6506

SCC's recommendations for handling the total and available cyanide results for the Alaskan Cruise Ship project samples are summarized in the table on the following page

Note: The results in the database are reported in the units provided by the laboratories that performed the analyses. Method OIA-1677 specifies reporting results in units of micrograms per liter (µg/L), whereas the older methods (335.2 and 335.3) specify reporting results in units of milligrams per liter (mg/L). However, for ease of comparison in the table the follows, the results for total cyanide have been converted to the same units as the available cyanide results, µg/L. "ND" indicates that cyanide was not detected. In these cases, the reported detection limit is shown in parentheses.

If you have any questions about the information in this memorandum or the cyanide results in the database, please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com.

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Summary of SCC Recommendations for Cyanide Results in the Alaskan Cruise Ship Project

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65207	Accommodations wastewater	ND (5)	15.7	Sample not treated with lead carbonate to remove sulfides. Low MS/MSD recoveries for total cyanide. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65211	Food pulper wastewater	14	88.4	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65219	Influent to treatment	ND (5)	10.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65227	Influent to treatment	ND (5)	7.54	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data for influents. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65231		ND (5)	35.4	
6503	65235		ND (5)	16	
6503	65261	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65265		ND (5)	5.86	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65273		ND (5)	ND (2)	Total cyanide qualified as minimum value.
6503	65281		ND (5)	8.96	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65283	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Sample not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65295	Source water	ND (5)	19.1	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65395	Galley wastewater	ND (5)	22.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65411	Food pulper	6	35.7	
6504	65455	Influent to treatment	ND (5)	26.9	
6504	65459	Influent to treatment	ND (5)	29	
6504	65463	Influent to treatment	ND (5)	11.7	
6504	65467	Influent to treatment	ND (5)	11.5	
6504	65471	Influent to treatment	ND (5)	11.6	
6505	65603	Galley wastewater	ND (5)	2.2	Total cyanide qualified as minimum value
6505	65659	Influent to treatment	ND (5)	30.7	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65731	Galley wastewater	ND (5)	12.9	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65745	Biosolids	11	15.2	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6506	65896	Influent to treatment	ND (5)	45.5	
6506	65900	Influent to treatment	ND (5)	36.2	
6506	65904	Influent to treatment	ND (5)	75.6	
6506	65908	Influent to treatment	ND (5)	72.2	
6506	65912	Influent to treatment	ND (5)	76.5	

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MEMORANDUM

DATE: January 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty, Ph.D.
Senior Scientist

SUBJECT: Summary of Telephone Conversation with the Available Cyanide Laboratory

At your suggestion, I contacted the laboratory that ran the available cyanide analyses for Episodes 6503 to 6506 and asked about cross-contamination concerns, glassware washing procedures, and other aspects of the analysis that might explain the discrepancies between the total and available cyanide results. I spoke with John Sebroski, the laboratory director at Bayer Material Science on January 19, 2005. John gave me the following information:

- All of the "glassware" involved in the analysis is disposable. This includes the cups on the autosampler, the tubing on the flow injection system, etc. They do not reuse any of it, so there are no washing issues.

- The design of the flow injection instrumentation minimizes any concerns about carryover because the sample is injected into a continuous flow of solution that runs through the analyzer.

- They do run frequent blanks on the instrument, especially after QC samples such as the lab control sample (LCS or OPR). Those QC samples are run at relatively high levels, and there is no evidence of carryover or memory effects in the blanks. (I also confirmed this prior to calling him, using the data for these four episodes.)

- The OIA-1677 method has an ASTM counterpart that uses the same technique. There is a 2004 version of the ASTM standard that addresses the potential for sulfide interferences by introducing a bismuth nitrate reagent into the system to remove sulfides. John indicated that the use of the bismuth nitrate reagent could easily be accommodated using Method OIA-1677, since the instrumentation is the same as the ASTM standard.

- John indicated that sulfide problems for total cyanide are always a significant issue. He also said that the flow injection system for available cyanide can detect (and be affected by) sulfides at a much lower level than the field test methods will detect. Therefore, any sample not treated with lead carbonate in the field may well have an interference for available cyanide, even if the field test was negative for sulfides.

In summary, my conversation with Mr. Sebroski confirms much of the information SCC summarized in our lengthy discussion of the issues surrounding the total and available cyanide results for this project and generally rules out the chance that analytical concerns, such as carryover or glassware cleaning procedures, as an explanation for the observed cyanide results. Please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com, if you have any questions.

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